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<p>During the project, we have investigated the linear and nonlinear response of two dimensional gold square-nanopatch arrays. We have shown that these arrays exhibit very narrow resonances corresponding to the formation of leaky modes associated with surface plasmons at the air/metal interfaces. The experimental measurements have confirmed the spectral behaviour predicted by the simulations and emphasized that fabrication tolerances, such as the roughness, do not noticeably affect the performance of the device since they broaden and shift slightly the plasmonic resonances. Then the potential sensitivity of the device has been experimentally derived by evaluating the spectral shift when an extremely small change of the refractive index is induced at the top surface of the sensor, leading to sensitivity values up to 1000 nm/RIU and a corresponding Figure of Merit (<i>FOM</i>) of 222 RIU-1 (<i>FWHM</i> of the resonance is only 4.5 nm). Moreover, we have shown a new, more intuitive path to detect variations of refractive index from colour changes. We compared the diffracted spectra of the same sample with air and an IPA solution on top, registering a significant change in the sample colour. This observation can be also quantified in terms of sensitivity, leading to $S = 121 \text{ nm/RIU}$ and $FOM = 6 \text{ RIU-1}$ (<i>FWHM</i> of the measured spectra is equal to 20 nm). Furthermore, such observation method allows establishing numerous other properties of the foreign compound such as its thickness or evaporation time, paving the way for new, yet unexplored plasmonic sensor devices. Finally the nonlinear response of the periodic arrays has been investigated and the effect of the geometrical parameters on the Surface Enhanced Raman Scattering signal has been analyzed.</p>						
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FINAL REPORT OF RESEARCH ACTIVITY

Principal Investigator's name: Dr. Marco Grande

Co-Principal Investigator's name: Dr. Tiziana Stomeo

Award no. W911NF-11-1-0284

1. Title

“Fabrication and characterization of two-dimensional periodic plasmonic nanostructures operating in linear and non-linear regime.”

2. Abstract

During the project, we have investigated the linear and nonlinear response of two-dimensional gold square-nanopatch arrays. We have shown that these arrays exhibit very narrow resonances corresponding to the formation of leaky modes associated with surface plasmons at the air/metal interfaces. The experimental measurements have confirmed the spectral behaviour predicted by the simulations and emphasized that fabrication tolerances, such as the roughness, do not noticeably affect the performance of the device since they broaden and shift slightly the plasmonic resonances.

Then the potential sensitivity of the device has been experimentally derived by evaluating the spectral shift when an extremely small change of the refractive index is induced at the top surface of the sensor, leading to sensitivity values up to 1000 nm/RIU and a corresponding Figure of Merit (FOM) of 222 RIU⁻¹ ($FWHM$ of the resonance is only 4.5 nm). Moreover, we have shown a new, more intuitive path to detect variations of refractive index from colour changes. We compared the diffracted spectra of the same sample with air and an IPA solution on top, registering a significant change in the sample colour. This observation can be also quantified in terms of sensitivity, leading to $S = 121$ nm/RIU and $FOM = 6$ RIU⁻¹ ($FWHM$ of the measured spectra is equal to 20 nm). Furthermore, such observation method allows establishing numerous other properties of the foreign compound such as its thickness or evaporation time, paving the way for new, yet unexplored plasmonic sensor devices. Finally the nonlinear response of the periodic arrays has been investigated and the effect of the geometrical parameters on the Surface Enhanced Raman Scattering signal has been analyzed.

Therefore the simple geometry, the insensitivity to the electric field polarization, the compatibility with cheaper nanotechnology processes (e.g. Nano-Imprinting Lithography), the possibility to use contemporaneously these devices in linear and nonlinear regimes make them very attractive as a powerful sensing integrated platform.

3. Report

This project aims to revisit the design, fabrication and characterization of two-dimensional periodic plasmonic nanostructures operating in linear and non-linear regime. In particular, during this period of this project, the Investigators have focused on the fabrication and the characterization of two-dimensional arrays of gold patches on both borosilicate glass and silicon substrates.

The sketch of the fabricated square plasmonic gold nano-patches is shown in Figure 1 where p , a and w indicate the periodicity, the slit aperture and the metal thickness, respectively.

We have fabricated square nanopatches in a two-dimensional square array since this configuration makes the device insensible to the polarization as reported in the previous report. Moreover the periodicity p has been properly chosen in order to design a plasmonic resonance at ~ 633 nm for the following nonlinear measurements. This condition can be achieved fixing the periodicity p equal to ~ 630 nm.

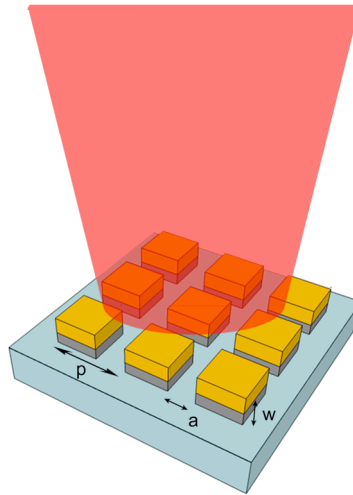


Figure 1: Sketch of the 2D square plasmonic gold nano-patches probed by a focused light: p , a and w indicate the periodicity, the slit aperture and the metal thickness, respectively.

The fabrication procedure of the 2D arrangement of gold square nano-patches involved three main processing steps and each one required an optimization and check process. The first step consisted of the optimization of the e-beam writing process on both silicon and borosilicate glass substrates. To define the geometry of our 2D pattern we have used a double layer Polymethyl-methacrylate (PMMA/MMA) resist, which is a positive resist and allows achieving a high quality *lift-off* process needed for defining metal nano-patches on both the samples. In particular, we used a thickness of 700 nm of bi-layer resist (PMMA/MMA). Since the borosilicate glass is an insulating substrate, before the deposition of the bi-layer resist, we covered it with a few nanometers of Chrome layer in order to avoid the charging effect which causes the deflection of the e-beam during the exposure leading up to the distortion of the pattern. The choice of the Cr layer instead of a different metal is due to the fact that the first one improves the adherence properties of gold layer on the glass. It is worth pointing out that the impact of the Cr adhesion

layer on the gold patch optical response is only related to a negligible red-shift of the overall resonance with the increase of the Cr thickness. The 2D plasmonic pattern was written by using a Raith150 e-beam lithography system (equipped with a Gemini Column) operating at 30 kV. A preliminary dose-test was performed to define the optimum layout since the actual size of the pattern is influenced by the electron dose. A proximity error correction (PEC) was also applied to accomplish this target and the final dose was determined through Scanning Electron Microscope (SEM) inspections at 10 kV. Subsequently the sample was developed in a Methyl-Isobutyl-Ketone (MIBK) solution and then rinsed in an Isopropyl alcohol-Methanol mixture. Isopropyl alcohol (IPA) solution was used as stopper for the development. Subsequently the 200 nm-thick gold layer was evaporated by means of a thermal evaporator with a current of 300 A and a deposition rate of 2 Å/sec. Finally, a lift-off process in an acetone bath was employed to remove the resist regions thus revealing that the two-dimensional nano-patch array dimensions correspond to the nominal numerical results.

Figure 2(a) and Figure 2(b) show the SEM micrographs of the final 2D gold nano-patches on borosilicate glass and silicon, respectively. The inspection of the images reveals square gold nano-patches with desired geometrical parameters. In Figure 2(a), the accelerating voltage of the SEM has been set equal to 5 kV since the borosilicate glass substrate gives rise to charge effects that limit the inspection time. In Figure 2(b) the resist-evaporated gold layer peeling off is shown during the lift-off process of the 2D gold nano-patches.

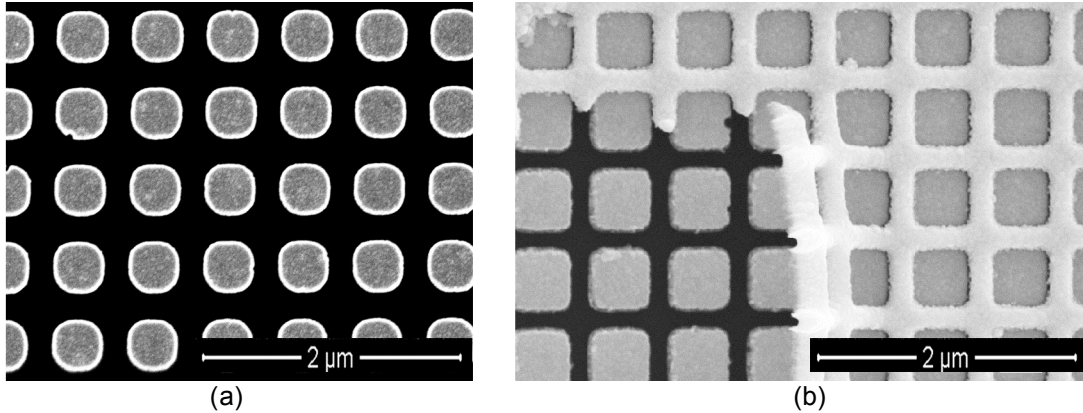


Figure 2: SEM micrograph for the 2D gold nanopatch array on (a) borosilicate glass and (b) silicon substrate. In (b) the resist-evaporated gold layer peeling off is shown during the lift-off process.

The fabricated devices have been characterized in the linear regime by means of an optical setup in the VIS-NIR range as reported in the previous reports.

Figure 3 shows a good agreement between the simulated and measured reflection spectra of the device on borosilicate glass with $p = 630$ nm and $a = 200$ nm. The measurements reveal a dip at about 640 nm that is slightly shifted with respect to the numerical findings. This discrepancy can be related to the rounded corners of the single nano-patch (as shown in Figure 2a) and to the gold film roughness that tends to smooth and broaden the resonances of the structure. Moreover the experimental results reveal the presence of the Fabry-Perot (FP)-like state corresponding to the dip at about 840

nm. The simulations also show that the reflection behaviour is almost the same when the slit aperture a is shrunk down to 120 nm. This shows that the device is not extremely sensitive to fabrication defects or errors.

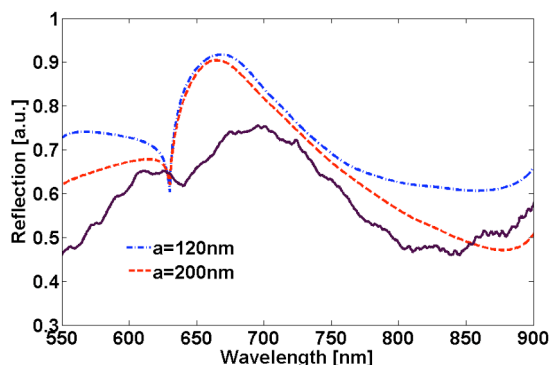


Figure 3: Comparison between experimental measurements (purple solid line) and the numerical results for the 2D array on borosilicate glass substrate when the slit aperture a is equal to 120 nm (dashed red line) and 200 nm (dashed-dot blue line), respectively.

Finally, we assessed the nonlinear response of the 2D nano-patch arrays on silicon substrate. These plasmonic devices have been inspected by functionalizing the metal surface by means of a conjugated rigid thiol, 4-methoxy-terphenyl-4''-methanethiol (TPMT), forming a very dense, closely packed, reproducible 18 Å-thick, self-assembled monolayer (SAM). The sample has been characterized by means of a Horiba Jobin-Yvon LabRAM HR-VIS micro-Raman spectrometer equipped with a 633 nm laser source filtered by a neutral density filters. Figure 4a reports the SERS signal of the sample with $p = 630$ nm when the slit aperture a is varied. It is worth stressing that the evaluation of the Enhancement Factor (EF) leads to a value equal to about $2 \cdot 10^5$ when the highest peak centred at 1603 cm^{-1} is considered. In order to verify our experimental results and develop a powerful tool to predict the efficiency of metal nanostructures for Raman-based application, we developed a model that takes into account the spontaneous response (SP) of the molecule. The numerical results shown in Figure 4b are in good agreement with the experimental measurements, confirming the enhancement of Raman response with the increasing aperture size of the metal grating. Similar results may be obtained using an approach where a system of Maxwell-Bloch equations is used to describe the Raman active medium, and Maxwell-Drude-Lorentz equations are used to model the remaining portions of the grating and substrate.

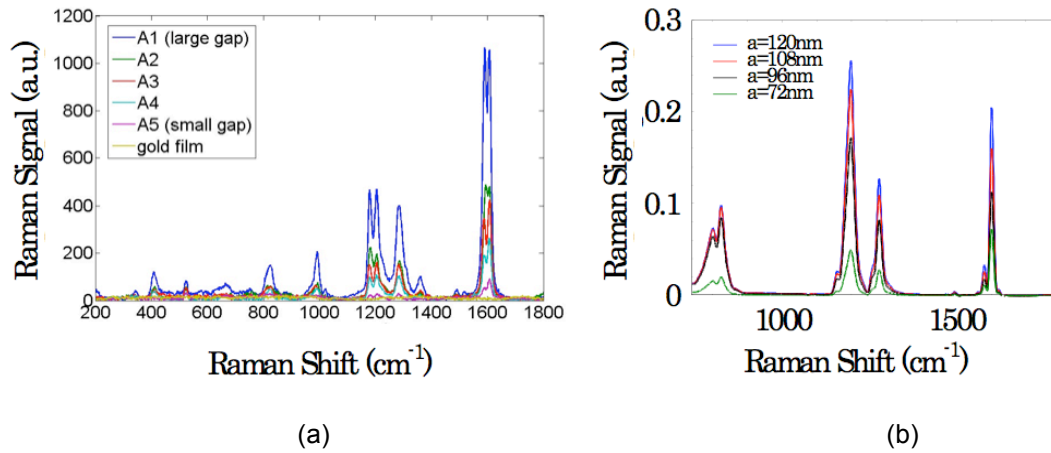


Fig.4: a) Experimental and b) simulated SERS signals when the slit aperture a is varied (the yellow curve in (a) corresponds to the reference signal of the flat gold film).

Publication list:

1. M. GRANDE, M.A. VINCENTI, T. STOMEIO, G. MOREA, R. MARANI, V. MARROCCO, V. PETRUZZELLI, A. D'ORAZIO, R. CINGOLANI, M. DE VITTORIO, D. DE CEGLIA, M. SCALORA, *"Experimental demonstration of a novel bio-sensing platform via plasmonic band gap formation in gold nano-patch arrays"*, Optics Express, Vol. 19, Issue 22, pp. 21385-21395 (2011).
2. M. GRANDE, M.A. VINCENTI, T. STOMEIO, G. MOREA, R. MARANI, V. MARROCCO, V. PETRUZZELLI, A. D'ORAZIO, R. CINGOLANI, M. DE VITTORIO, D. DE CEGLIA, M. SCALORA, *"Experimental demonstration of a novel bio-sensing platform via plasmonic band gap formation in gold nano-patch arrays"*, Virtual Journal of Biomedical Optics, Vol 6, pp21385 (2011) (selected for publication in VJBO);
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5. M. GRANDE, M.A. VINCENTI, T. STOMEIO, G. V. BIANCO, D. DE CEGLIA, G. MOREA, R. MARANI, V. MARROCCO, V. PETRUZZELLI, M. DE VITTORIO, G. BRUNO, M. SCALORA, A. D'ORAZIO, *"Novel plasmonic bio-sensing system based on two-dimensional gold patch arrays for linear and nonlinear regimes"*, Advances in Science and Technology Vol. 81 (2013) pp 15-19;
6. M. GRANDE, G. V. BIANCO, M. A. VINCENTI, D. DE CEGLIA, V. PETRUZZELLI, M. SCALORA, G. BRUNO, A. D'ORAZIO, M. DE VITTORIO AND T. STOMEIO, *"2D plasmonic gold nano-patches for linear and nonlinear applications"*, submitted to Microelectronic Engineering.